degree of dissociation of 13 percent solution have been calculated and recorded in Table II. These results are also

TABLE II.

PERCENT CONCENTRATION	13	21	28	34
RELATIVE DEGREE OF DISSOCIATION	1.00	0.84	0.68	0.82

shown as a curve (Fig. 1) with the degree of dissociation plotted against the concentration. From this curve the progressive dissociation of the HSO_4^- ion is clearly seen. No lines attributable to the undissociated $KHSO_4$ molecule were observed even in the most concentrated solution. The fact that no undissociated molecules are present in solution is characteristic of normal salts, while the fact that the HSO_4^- ion dissociates progressively is characteristic of acids. Thus the Raman method of investigation indicates that $KHSO_4$ has characteristics common to both acids and normal salts as would be inferred from chemical considerations.

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Quantum Mechanics and the Third Law of Thermodynamics

Rodebush[1] has recently discussed certain points concerning the third law of thermodynamics in terms of quantum mechanics. His recognition of the significance of quantum mechanics in considering the behavior of solutions and glasses at low temperatures we believe to be of interest, and we agree with the more important of his conclusions. However, there have arisen some questions of interpretation in which we differ from the statements of his paper. We have thought it of value to present here, as explicitly as possible and at the risk of some duplication of ideas, an outline of these points and a discussion of their bearing on the expected behavior of the systems under treatment. It is our opinion that the views presented below have been in the main accepted by investigators interested in the theory of the third law; however, so far as we are aware no equivalent discussion has been published.

Without entering into the question of the relation between statistical mechanics and thermodynamics, we accept as giving a value for the entropy of the system in which we are interested the expression $k \ln N$, in which N is the number of independent wave functions for the system compatible with our knowledge as to its condition. Following the plan adopted by Rodebush, we first discuss the case of an optically active substance.[2] An isolated molecule of such a substance in its lowest rotational and vibrational state and known to be in the dextro configuration[3] is to be represented by a single wave function corresponding to this configuration, and will have the quantum weight 1, and not 2. On the other hand, if the molecule is in one of the two lowest energy states corresponding to the accurate solution of the wave equation (as could be determined by an energy measurement extending over a period of time long compared to the time required for spontaneous dextro-levo conversion), it is to be represented by a single wave function which is either symmetric or antisymmetric relative to inversion about a center, and which is formed by linear combination of the dextro and levo wave functions. It will then not be known whether the molecule is a dextro or a levo molecule. Only in the case that neither its optical activity nor its (exact) energy is known can we assign to it the quantum weight 2.

By analogy with the simple case of the optical isomers Rodebush generalizes the many-minima problem exemplified by glasses and crystalline solutions with the following statement. "We have a number of configurations of the same energy separated by energy crests. By symmetric and antisymmetric linear combinations of wave functions,[4] we obtain a total number of wave functions equal to the degeneracy; that is to say, the total number of configurations having the same energy. Thus, instead of each configuration having a distinct energy, each configuration has now a large number of closely spaced energy levels."

Here we prefer to state the situation in a somewhat different way, as follows. The system in its low temperature condition and known to have a particular configuration[5] (one of N possible configurations) is to be represented by one of an appropriate set of N wave functions, corresponding to the N configurations. If not the configuration, but the energy of the system is to be investigated with great accuracy, by means of observations extending over a very long period of time, the set of wave functions of interest is that corresponding to accurate solution of the wave equation (these wave functions being linear combinations of those corresponding to the N configurations). The energy value found by experiment would be one of the multiplet of N levels corresponding to the low temperature condition. We cannot, however, make use of the two sets of wave functions simultaneously, but must use either the configuration wave functions or the multiplet wave functions, or some other equivalent set. In other words, both the configuration and the exact energy of the system cannot be simultaneously known. If either is known a single wave function (of the set of N) is sufficient to describe the system and the system will then have the quantum weight 1, and not N. However, if neither the configuration nor the exact energy of the system is known, we may use either set of N wave functions (or any other set formed from them by linear combinations) to describe it, and its quantum weight will then be N.

The behavior of systems on cooling to a very low temperature ($kT \ll h\nu$, where ν is the frequency of the lowest oscillational state) may be outlined in the case of an ideal solution somewhat as follows.[6] If ν^* is the frequency of transition among the various configurations (as given by the corresponding resonance integral divided by h), the

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energy spread of the multiplet levels will be of the order of $h\nu^*$. If the cooling be done so slowly that a time very long compared to $1/\nu^*$ is allowed at each temperature, the loss of heat will be such as to correspond to a loss of entropy of $k \ln N$, since the multiplet levels under such conditions may be regarded as discrete. On rapid cooling to the same low temperature, the energy of the system will be determinable only to within about $h/2\pi\tau$, where τ is the time of observation at the temperature in question. If this uncertainty in energy is large compared to $h\nu^*$ there will still remain N states (N independent wave functions) of the system falling within the observable energy limits, and the entropy will be $k \ln N$. Only after a long time of observation at this temperature can these limits be narrowed sufficiently to permit the statement that a single state is represented and the entropy is zero.

A real solution or glass differs from an ideal solution or glass, discussed above, in that one of its configurations, corresponding to a pure crystalline substance or a mixture of pure crystalline substances, possesses an energy lower than any other. If such a system be subjected to very slow cooling, or be held for a long time at a low temperature as discussed above, it will ultimately attain this configuration (mainly by transition through excited vibrational states rather than by penetration of potential barriers), and will therefore have zero entropy. On cooling sufficiently rapidly to exclude effectively transitions between configurations, or on holding at the low temperature for a time shorter than required for these transitions to occur, the multiplicity N will be retained by the system, its entropy then remaining greater than zero.

It may be pointed out that the discussion of the entropy of a real solution or glass on the basis of quantum mechanics, as just given, is identical with the discussion of the problem in the pre-quantum-mechanical era. On the other hand, the quantum mechanics has introduced a significant change in the discussion of the entropy of an ideal solution or glass. Before the development of quantum mechanics there was no conceivable mechanism leading to the loss of the final $k \ln N$ of entropy at very low temperatures for an ideal solution or glass, defined as having N configurations with exactly the same energy. The quantum-mechanical mechanism leading to the loss of this entropy is the resonance of the system among the N configurations.

Rodebush has also implied that the accuracy with which very low temperatures can be measured is restricted by the uncertainty principle and by the nature of the substance under investigation. However, the accuracy of a temperature measurement is not limited in a serious way by the uncertainty principle for energy, inasmuch as the relation between the uncertainty in temperature and the length of time involved in the measurement depends on the size of the thermometer, and the uncertainty in temperature can be made arbitrarily small by sufficiently increasing the size of the thermometer; we assume as the temperature of the substance the temperature of the surrounding thermostat with which it is in either stable or metastable equilibrium, provided that thermal equilibrium effective for the time of the investigation is reached.

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[1] W. H. Rodebush, J. Chem. Phys. **2**, 669 (1934).
[2] For a thorough discussion of this see F. Hund, Zeits. f. Physik **43**, 805 (1927).
[3] We shall use the word configuration in this paper to represent the approximate relative spatial arrangement of the nuclei of the atoms in the system under consideration (neglecting the effect of the vibrational motion on the nuclear positions).
[4] At the request of Professor Rodebush, the wording of this sentence has been changed slightly from that in his paper.
[5] We assume each configuration to be in its lowest vibrational state.
[6] We believe that the ideas discussed in this connection parallel those of Rodebush, but have thought it worth while to give them in greater detail.

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